

**Subject: Re: [NTP Web] NTP Nomination of Diazonaphthoquinone Esters**

**Date:** Monday, April 24, 2006 1:33 PM

**From:** James.Lockard@AZ-EM.com

**To:** "Masten, Scott (NIH/NIEHS)" <masten@niehs.nih.gov>

**Conversation:** [NTP Web] NTP Nomination of Diazonaphthoquinone Esters

Scott,

As promised, attached is the WORD file that you sent to me, annotated to clarify apparent and possible errors and misunderstandings. All of these notes are from my knowledge of the chemicals and the industry. I gathered this knowledge during perhaps 21 years as the Product Safety Manager for the photoresist business area of what is now AZ Electronic Materials USA Corp.(AZ) , formerly part of Hoechst Celanese Corporation and Clariant Corporation.

AZ is the supplier of the only commercial photoresists mentioned in the document. There are at least two other suppliers to the US market of products containing the listed DNQ esters, at least one of which probably exceeds our volumes. Note that these DNQ esters were the photoactive compounds, PACs, in perhaps the first two commercial liquid positive photoresists, introduced in the 1970's and 1980. To our knowledge, they are not used in any advanced photoresists. They do, however, continue to be used in small, but significant, volume today.

Also attached is a spreadsheet of old toxicity testing results from our records. The only report that we actually have in our US files that is in English is the 1982 Ames test for 68510-93-0.

(See attached file: DNQs CIRD\_sec2-10 AZ Electronic Materials Comment.doc)

(See attached file: DNQ Test Results for NTP 0406.xls)

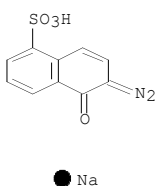
If you have further questions please feel free to contact me.

Best regards.

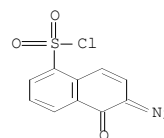
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**2.0 Introduction** (In the Executive Summary and Section 1.0 Basis for Nomination, it is implied that these materials are used in I-line photoresists. The two precursors are not used in photoresists at all, to our knowledge. The two DNQ esters are used exclusively in G-line photoresists, earlier technology to the I-line photoresists. Their functional properties and particularly their absorbance/bleaching characteristics at I-line (365 nm) make them unsuitable for commercial photoresists. G-line photoresists were the original technology and have been in strong decline for various technical reasons since the late 1980's. We, AZ Electronic Materials USA Corp., expect that neither of these DNQ esters will be included in 2006 TSCA IUR reporting. The Executive Summary states that DNQ esters are soluble in organic solvents and insoluble in aqueous alkaline solutions. In fact these are quite high molecular weight molecules that are isolated as amorphous solids. Most are only metastable in organic solvents. Stability is enhanced by the novolak resins used in the photoresists. Otherwise the DNQ esters crystallize in hours or days to give a highly insoluble solid. As high molecular weight organics, the water solubility of the DNQ esters is zero, thus absorption is expected to be zero. They are decomposed by aqueous base except for dilute base. Thus, residual DNQ esters in developing photoresists would be decomposed, but if they were to reach a diluted waste stream, they may be stable in suspension. This last is beyond our direct experience.)

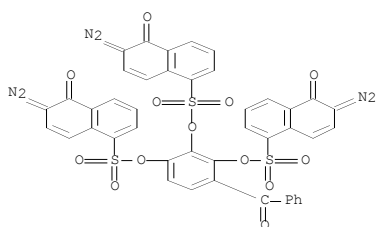
Sodium 1,2-naphthoquinonediazide-5-sulfonate  
[2657-00-3]



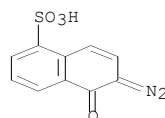
1,2-Naphthoquinonediazide-5-sulfonyl chloride  
[3770-97-6]



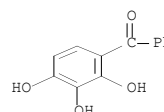
2,3,4-Trihydroxybenzophenone tris(1,2-naphthoquinonediazide-5-sulfonate)  
[5610-94-6]



2,3,4-Trihydroxybenzophenone 1,2-naphthoquinonediazide-5-sulfonate  
[68510-93-0]



(Typical degree of esterification  
1.7-2)



The CASRN for 2,3,4-trihydroxybenzophenone 1,2-naphthoquinonediazide-5-sulfonate may be considered generic for the following isomers:

- 2,3,4-trihydroxybenzophenone tris(1,2-naphthoquinonediazide-5-sulfonate);
- 2,3,4-trihydroxybenzophenone 4-(6-diazo-5,6-dihydro-5-oxo-1-naphthalenesulfonate);
- 2,3,4-trihydroxybenzophenone 3-(6-diazo-5,6-dihydro-5-oxo-1-naphthalenesulfonate);
- 2,3,4-trihydroxybenzophenone 2-(6-diazo-5,6-dihydro-5-oxo-1-naphthalenesulfonate);
- 2,3,4-trihydroxybenzophenone 3,4-bis(6-diazo-5,6-dihydro-5-oxo-1-naphthalenesulfonate);

- 2,3,4-trihydroxybenzophenone 2,3-bis(6-diazo-5,6-dihydro-5-oxo-1-naphthalenesulfonate); and
- 2,3,4-trihydroxybenzophenone 2,4-bis(6-diazo-5,6-dihydro-5-oxo-1-naphthalenesulfonate).

## 2.1 Chemical Identification and Analysis

### 2.1.1 Sodium 1,2-naphthoquinonediazide-5-sulfonate

Sodium 1,2-naphthoquinonediazide-5-sulfonate ( $[C_{10}H_6N_2O_4S \cdot Na]$ ; mol. wt. = 273.24) is also called:

NA 125

1-Naphthalenesulfonic acid, 6-diazo-5,6-dihydro-5-oxo, sodium salt (7CI, 8CI, 9CI)

Sodium 1,2-naphthoquinone-2-diazide-5-sulfonate

Sodium 2,1-diazonaphthol-5-sulfonate

Sodium 2-diazo-1-hydroxynaphthalene-5-sulfonate

Sodium 2-diazo-1-naphthol-5-sulfonate

Sodium 2-diazo-1-oxo-1,2-dihydronaphthalene-5-sulfonate

Sources: IMO (undated); Registry (2002)

### 2.1.2 Sodium 1,2-naphthoquinonediazide-5-sulfonyl chloride

1,2-Naphthoquinonediazide-5-sulfonyl chloride ( $[C_{10}H_5ClN_2O_3S]$ ; mol. wt. = 268.68) is also called:

1-Hydroxy-5-chlorosulfonyl-2-naphthalenediazonium hydroxide, inner salt

1-Naphthalenesulfonyl chloride, 6-diazo-5,6-dihydro-5-oxo (6CI, 7CI, 8CI, 9CI)

1,2-Naphthoquinone-2-diazide-5-sulfonyl chloride

1,2-Naphthoquinonediazido-5-sulfonyl chloride

1-Oxo-1,2-dihydro-2-diazonaphthalene-5-sulfonyl chloride

1-Oxo-2-diazonaphthoquinone-5-sulfonyl chloride

2-Diazo-1-naphtho-5-sulfonyl chloride

2-Diazo-1-naphthol-5-sulfonyl chloride

2-Diazo-1-naphthone-5-sulfonic acid chloride

2-Diazo-1-naphthone-5-sulfonyl chloride

2-Diazo-1-oxo-1,2-dihydronaphthalene-5-sulfonyl chloride

2-Diazo-1-oxonaphthalene-5-sulfonyl chloride

2-Diazo-1(2H)-naphthalenone-5-sulfonyl chloride

2-Diazo-1,2-dihydro-1-oxonaphthalene-5-sulfonyl chloride

2-Diazo-1,2-naphthoquinone-5-sulfonyl chloride

3-Diazo-4-oxo-1-naphthalenesulfonyl chloride ([This is 4-sulfo, not 5-sulfo](#))

5-(Chlorosulfonyl)-1,2-naphthoquinone-2-diazide

6-Diazo-5,6-dihydro-5-oxo-1-naphthalenesulfonyl chloride

6-Diazo-5,6-dihydro-5-oxonaphthalene-2-sulfonyl chloride ([This is 7-sulfo, not 5-sulfo](#))

6-Diazo-5-hydroxy-1-naphthalenesulfonyl chloride

6-Diazo-5-oxo-1-naphthalenesulfonyl chloride

Naphthoquinone-(1,2)-diazido-(2)-5-sulfonyl chloride

o-Naphthoquinonediazide-5-sulfonyl chloride ([Ambiguous old name](#))

Sources: MSDS-OHS (2001a); Registry (2002)

### 2.1.3 2,3,4-Trihydroxybenzophenone tris(1,2-naphthoquinonediazide-5-sulfonate)

2,3,4-Trihydroxybenzophenone tris(1,2-naphthoquinonediazide-5-sulfonate) ( $[C_{43}H_{22}N_6O_{13}S_3]$ ; mol. wt. = 926.88) is also called:

Benzophenone, 2,3,4-trihydroxy-, tris(6-diazo-5,6-dihydro-5-oxo-1-naphthalenesulfonate) (8CI)  
 1-Naphthalenesulfonic acid, 6-diazo-5,6-dihydro-5-oxo-, 4-benzoyl-1,2,3-benzenetriyl ester (9CI)  
 1-Naphthalenesulfonic acid, 6-diazo-5,6-dihydro-5-oxo-, triester with 2,3,4-trihydroxybenzophenone (7CI, 8CI)  
 2,1,5-Diazonaphthoquinone ester with 2,3,4-trihydroxybenzophenone  
 2,3,4-Trihydroxybenzophenone 1,2-naphthoquinone-2-diazide-5-sulfonic acid triester  
 2,3,4-Trihydroxybenzophenone naphthoquinone-1,2-diazide-5-sulfonic acid ester (1:3)  
 2,3,4-Trihydroxybenzophenone tris(1,2-naphthoquinone-2-diazide-5-sulfonate)  
 2,3,4-Tris(1,2-naphthoquinone-2-diazido-5-sulfonyloxy)benzophenone  
 2,3,4-Tris(1-oxo-2-diazonaphthoquinone-5-sulfonyloxy)benzophenone  
 6-Diazo-5,6-dihydro-5-oxo-1-naphthalenesulfonic acid, 4-benzoyl-1,2,3-benzenetriyl ester  
 6-Diazo-5,6-dihydro-5-oxo-1-naphthalenesulfonic acid, triester with 2,3,4-trihydroxybenzophenone  
 NT 300  
 NT Ester-5-sulfonic acid  
 PAC III

Sources: MSDS-OHS (2001b); Registry (2002)

#### 2.1.4 2,3,4-Trihydroxybenzophenone 1,2-naphthoquinonediazide-5-sulfonate

2,3,4-Trihydroxybenzophenone 1,2-naphthoquinonediazide-5-sulfonate ( $[C_{13}H_{10}O_4 \times C_{10}H_6N_2O_4S]$ ; mol. wt. = 250.25 [\(Inconsistent with given molecular formula\)](#)) is also called:

1-Naphthalenesulfonic acid, 6-diazo-5,6-dihydro-5-oxo-, ester with phenyl(2,3,4-trihydroxyphenyl)methanone (9CI)  
 1,2-Naphthoquinonediazido-5-sulfonyl chloride 2,3,4-trihydroxybenzophenone ester  
 2,1,5-Diazonaphthoquinone sulfonic acid, ester with 2,3,4-trihydroxy benzophenone  
 2,3,4-Trihydroxybenzophenone 1,2-naphthoquinone-2-diazide-5-sulfonate  
 2,3,4-Trihydroxybenzophenone 1,2-naphthoquinonediazido-5-sulfonate  
 2,3,4-Trihydroxybenzophenone 1,2-naphthoquinonediazide-5-sulfonic acid ester  
 2,3,4-Trihydroxybenzophenone 1-naphthoquinone-2-diazide-5-sulfonyl chloride ester  
 2,3,4-Trihydroxybenzophenone ester with 1,2-naphthoquinonediazide-5-sulfonic acid  
 2,3,4-Trihydroxybenzophenone ester with 1,2-naphthoquinonediazido-5-sulfonyl chloride  
 2,3,4-Trihydroxybenzophenone ester with naphthoquinone-1,2-diazido-5-sulfonyl chloride (1:2:5)  
 2,3,4-Trihydroxybenzophenone naphthoquinone-(1,2)-diazide-(2)-5-sulfonic acid ester  
 2,3,4-Trihydroxybenzophenone naphthoquinone-1,2-diazido-5-sulfonate  
 2,3,4-Trihydroxybenzophenone *o*-naphthoquinonediazide-5-sulfonyl chloride ester  
 2,3,4-Trihydroxybenzophenone-1,2-naphthoquinonediazido-5-sulfonic acid ester  
 2,3,4-Trihydroxybenzophenone-1-oxo-2-diazonaphthoquinone-5-sulfonate  
 NOD  
 NT 200  
 THBP 215

Sources: MSDS-OHS (2001c); Registry (2002)

2,3,4-Trihydroxybenzophenone tris(1,2-naphthoquinonediazide-5-sulfonate) and the six other possible 2,1-diazonaphthoquinone-5-sulfonates of 2,3,4-trihydroxybenzophenone have been isolated and characterized by infrared (IR), chromatography (e.g., high-performance liquid chromatography [HPLC]), and advanced nuclear magnetic resonance (NMR) techniques (DiCarlo et al., 1994).

## 2.2 Physical-Chemical Properties

Property	Information	Reference(s)
<i>1,2-Naphthoquinonediazide-5-sulfonyl chloride</i>		
Physical State	orange solid	MSDS-OHS (2001a)
Odor	odorless	MSDS-OHS (2001a)
Decomposition Point (°C)	100	MSDS-OHS (2001a)
	113	Chinamarket (1998)
Soluble in:	dioxane and acetone	Chinamarket (1998)
Insoluble in:	water	Chinamarket (1998)
<i>2,3,4-Trihydroxybenzophenone tris(1,2-naphthoquinonediazide-5-sulfonate)</i>		
Physical State	solid or powder	MSDS-OHS (2001b)
<i>2,3,4-Trihydroxybenzophenone 1,2-naphthoquinonediazide-5-sulfonate</i>		
Physical State	liquid	MSDS-OHS (2001c)

1,2-Naphthoquinonediazide-5-sulfonyl chloride is a flammable solid; dust or air mixtures of the substance may ignite or explode. The compound may decompose when in contact with air, light, moisture, heat, or storage and use above room temperature, releasing toxic, corrosive, flammable, or explosive gases. Thermal decomposition products include oxides of carbon, sulfur, nitrogen, and acid halides ([This is MSDS boilerplate for high temperature air thermolysis, i.e. burning. These readily decompose at lower temperature to makes black smoke and black tar](#)). It is incompatible with alkaline ([this is important](#)) and oxidizing materials ([this is not important](#)) (MSDS-OHS, 2001a).

2,3,4-Trihydroxybenzophenone tris(1,2-naphthoquinonediazide-5-sulfonate) and 2,3,4-trihydroxybenzophenone 1,2-naphthoquinonediazide-5-sulfonate are stable at normal temperatures and pressure. Thermal decomposition products are oxides of carbon. Both compounds are incompatible with oxidizing materials, resulting in a fire or explosion. In addition, dust or air mixtures of 2,3,4-trihydroxybenzophenone tris(1,2-naphthoquinonediazide-5-sulfonate) may ignite or explode. Explosion may also occur if 2,3,4-trihydroxybenzophenone 1,2-naphthoquinonediazide-5-sulfonate is exposed to heat (MSDS-OHS, 2001b,c). ([The trisester, 5610-94-6, and many others do not qualify as explosives except in Germany where the test is slightly more vigorous. They must be shipped in Germany with a diluent. Most DNQ esters will burst a container if heated to 100 C under confinement. All reactions are relatively slow and mild and do not approach the definition of detonation. Dust explosions are not considered a big issue based on the typical granular nature of the isolated solid.](#))

The sensitizers for the positive photoresists are usually the derivatives of DNQ. DNQ sulfonates, which are soluble in organic solvents and insoluble in aqueous alkaline solutions, undergo a number of reactions on exposure to light, ultimately resulting in the formation of substituted indene carboxylic acid. This acid, unlike the starting DNQ, is readily soluble in aqueous alkaline solutions. The five-substituted derivatives of DNQ, found to be the best for preparing the positive photoresists, exhibit a strong absorption at the wavelengths of mercury emission lines of 365 nm and 405 nm and a lower absorption at 436 nm (Bednar et al., 1993). ([We believe that the two esters listed, 5610-94-6 and 68510-93-0, are used exclusively in early technology G-line photoresists. They are not used in I-line resists at all.](#))

## 2.3 Commercial Availability

### Sodium 1,2-naphthoquinonediazide-5-sulfonate

Sodium 1,2-naphthoquinonediazide-5-sulfonate is supplied by ChemDesign Corporation (Fitchburg, MA) and MRI International (Newton, NJ) (Chemyclopedia Online, 2004). Diazo chemistry is a specialty of ChemDesign Corporation, a member of the Bayer custom services group; chemicals are produced in 1000- to 4000-gallon reactors (Bayer US, undated). The compound is also available in the United States from the following suppliers listed in the CHEMCATS database: ChemPacific USA Sales Marketing and Research Center (Baltimore, MD) (bulk quantities); Fluka Chemical Corporation (Ronkonkoma, NY) (100- and 500-g quantities with a purity  $\geq 97\%$ ); Pfaltz and Bauer, Inc. (Waterbury, CT) (50-g quantities with a purity of 98%); Monomer-Polymer and Dajack Laboratories, Inc. (Feasterville, PA); and TCI America (Portland, OR) (ChemPacific USA, 2001; Fluka Chem. Corp., 2001; Pfaltz and Bauer, Inc., 1999a; Monomer-Polymer and Dajack Laboratories, Inc., 1998; TCI America, 2000a). Under the 1998 and 2002 Inventory Update Rule (IUR), Specialty Chemical Products Corporation was listed as a company manufacturing or importing sodium 1,2-naphthoquinonediazide-5-sulfonate (U.S. EPA, 2004). It is also produced by Esprix Technologies (Sarasota, FL) as Diazo 10 (Esprix Technologies, 1998). PC Associates Inc. (Livingston, NJ) is a manufacturer and world-wide distributor of the salt (monohydrate) with 95% minimum purity (PC Associates Inc., 2001). (As far as we know there are only two actual manufacturers of this material, one German and one Japanese. Everyone in the US either imports the material or buys it from someone who imports the material.)

### 1,2-Naphthoquinonediazide-5-sulfonyl chloride

Pfaltz and Bauer, Inc. (Waterbury, CT) supplies 10-gram to 5-kilogram quantities of 2-diazo-1,2-naphthoquinone-5-sulfonyl chloride (Pfaltz and Bauer, Inc., 1999b). It is also available from ChemDesign Corporation (Fitchburg, MA), MRI International (Newton, NJ), and TCI America (Portland, OR) (Chemyclopedia Online, 2004; TCI America, 2000b). Under the 1998 and 2002 IUR, ChemDesign Corporation and Arch Chemicals, Inc. were listed, respectively, as companies manufacturing or importing the compound (U.S. EPA, 2004).

### 2,3,4-Trihydroxybenzophenone tris(1,2-naphthoquinonediazide-5-sulfonate)

No U.S. producers or suppliers were found. We import this material, well under the IUR reporting threshold.

### 2,3,4-Trihydroxybenzophenone 1,2-naphthoquinonediazide-5-sulfonate

Under the 1998 and 2002 IUR, ChemDesign Corporation and Arch Chemicals, Inc. were listed, respectively, as companies manufacturing or importing 2,3,4-trihydroxybenzophenone 1,2-naphthoquinonediazide-5-sulfonate (U.S. EPA, 2004). Diversitec Corporation (Fort Collins, CO), a manufacturer of chemicals used in graphic arts, can produce esters of 1,2-naphthoquinone-2-diazide-5-sulfonic acid with 2,3,4-trihydroxybenzophenone to the degree of substitution required by a customer (Diversitec Corporation, 1999). (We import this material, well under the IUR reporting threshold.)

## 3.0 Production Processes

The production of a 1,2-naphthoquinone-2-diazide or a sulfo-substituted compound thereof from a 2-diazo-1-naphthalene-sulfonic acid or a sulfo-substituted compound thereof can be obtained



using an aqueous alkaline solution containing iodine, an aqueous alkaline solution containing iodine dissolved in an organic solvent, or an aqueous alkaline solution containing an oxidizing agent and iodine or an iodine compound. The method provides good yields and gives a photoresist component free of contaminants. Diazotization and treatment of 2-amino-1,5-naphthalene disulfonic acid mono-sodium salt with sodium hydroxide and iodine produced 88.1% of sodium 1,2-naphthoquinone-2-diazide-5-sulfonate (Iida et al., 1999).

The relative amounts of trihydroxybenzophenone isomers formed during esterification with 1,2-naphthoquinonediazide-5-sulfonyl chloride depend on solvent polarity, base, reactant concentration, and reaction time. The proportions of the esters in the mixtures resulting from different reaction conditions equilibrated in the presence of base and 2,3,4-trihydroxybenzophenone to give a common mixture (Zampini et al., 1996). Naphthoquinonediazide derivative photosensitive compounds for positive resists can be prepared by condensation of phenolic OH-containing compounds with 1,2-naphthoquinonediazide-5-sulfonyl chloride in organic solvents by using dibasic amines (Shimosaki et al., 2001).

#### 4.0 Production and Import Volumes

Under the 1986, 1990, 1994, 1998, and 2002 Inventory Update Rule (IUR), an aggregate production volume ranging between 10,000 lb (4535.9 kg) and 500,000 lb (226,800 kg) was reported for sodium 1,2-naphthoquinone-2-diazide-5-sulfonate, 1,2-naphthoquinone-2-diazide-5-sulfonyl chloride, and 2,3,4-trihydroxybenzophenone 1,2-naphthoquinonediazide-5-sulfonate [\(Based on IUR data and our knowledge of the market, total US use likely does not significantly exceed 20,000 lb.\)](#). In 1986 and 1990, the same range was reported for 2,3,4-trihydroxybenzophenone tris(1,2-naphthoquinonediazide-5-sulfonate) (U.S. EPA, 2004). Additionally, 2,3,4-trihydroxybenzo-phenone tris(1,2-naphthoquinonediazide-5-sulfonate) was listed among the 262 non-high production volume (HPV) potentially persistent chemicals for which the Interagency Testing Committee (ITC) solicited voluntary submission of use and exposure data in its 45<sup>th</sup> report to the EPA Administrator (TSCA-ITC, undated).

#### 5.0 Uses

The majority of positive DNQ/novolak-based photoresists use mixtures of various DNQ-esters and positional isomers as the photoactive compounds (PACs). The condensation reaction of DNQ sulfonyl chloride with the polyhydroxylated ballast group can be highly regioselective, producing mixtures strongly favoring either even- or odd-numbered isomers (e.g., from triesters to octaesters) (Pandya et al., 1994). The five-substituted derivatives of DNQ were found to be the best for preparing the positive photoresists (Bednar et al., 1993).

##### Sodium 1,2-naphthoquinonediazide-5-sulfonate

Sodium 1,2-naphthoquinonediazide-5-sulfonate is a component of a polymer film for use as a near-field write-once memory medium (Kawai et al., 2001). It is used in the manufacture of presensitized printing plates and in the photosensitive layer for the production of waterless lithographic printing plate master (Goto et al., 1997; Kizu et al., 1996).

##### 1,2-Naphthoquinonediazide-5-sulfonyl chloride

1,2-Naphthoquinonediazide-5-sulfonyl chloride is manufactured for lithographic applications (Marks, 2001). Numerous Japanese patents exist for the compound. It is a component of

radiation-sensitive resin compositions for positive-working resists, semiconductor device fabrication, and for the manufacture of electronic parts, providing improved dry etching resistance and high-resolution patterns (Akiyama et al., 2001; Fujita et al., 2001; Kawahata et al., 2000; Nunomura et al., 2001; Takahashi, 2000). The composition protects film for color filter or spacer associated with intermediate electric insulator film among thin film transistors (Takeuchi et al., 2000). It is used for photolithography for forming intermediate electric insulator film and microlens; the microlens shows improved heat and solvent resistance, transparency, adhesion to substrate, and storage stability (Nishimura et al., 2000). As a reactant in heat-resistant photoresist resin composition, it provides controlled composition viscosity (Tomikawa et al., 2001). When used for positive-working light-sensitive resin composition containing organosilicon compounds, it creates a heat-resistant polyimide (Sasaki et al., 2001). Additionally, the compound can be used as an explosive (UTA, undated). (We are not aware of any significant volume in any of these uses. The chemical is reactive and would lead to very short shelf life of a commercial formulation.)

#### 2,3,4-Trihydroxybenzophenone tris(1,2-naphthoquinonediazide-5-sulfonate)

Diazonaphthoquinonesulfonic esters [5610-94-6] are ≤5 weight percent in the products AZ(R) P4110 Photoresist and AZ(R) P4620 Photoresist available from Clariant Corporation (Somerville, NJ) (Clariant Corporation, 2000, 2001; Hoechst Celanese, 1989b, 1994a). It is also found in the following photoresists supplied by Clariant: AZ 1915 (incorrect), AZ 5214 (incorrect), AZ EXP PLP 100XT (incorrect), AZ P4210, AZ P4400, AZ P4620, and AZ(R) EXP P4903 (Georgia Tech Microelectronics Research Center, undated). [Note: In 1997, the specialty chemicals business of Hoechst AG merged with Clariant AG of Switzerland (Hoechst AG, undated).] (Further note: In 2004 our business was purchased by Carlyle and set up as an independent company, AZ Electronic Materials USA Corp.)

#### 2,3,4-Trihydroxybenzophenone 1,2-naphthoquinonediazide-5-sulfonate

2,3,4-Trihydroxybenzophenone 1,2-naphthoquinonediazide-5-sulfonate is an ingredient in the following photoresists produced by Hoechst Celanese Corporation (Somerville, NJ): AZ 1350J-SF, AZ 1350B-SF, and AZ 1370-SF (These photoresists were phased out in the late 1980's and early 1990's, replaced by similar formulations in a safer solvent, which we still sell in small but significant volume.) (Hoechst Celanese, 1989a, 1994b,c). [Note: The CASRN for 2,3,4-trihydroxybenzophenone 1,2-naphthoquinonediazide-5-sulfonate, which may be considered generic for any of seven isomers, may be a better choice than 5610-94-6 for the esters designated in the photoresist compositions listed in Georgia Tech Microelectronics Research Center (undated).] (True, this is the CAS # we submitted to the Initial TSCA Inventory)

### **6.0 Environmental Occurrence and Persistence**

Total organic carbon from raw industrial wastewater from large-scale integrated circuit photoresist processing, containing 1,2-naphthoquinone-2-diazido-5-sulfonic acid sodium salt (Any DNQ in the "light" areas that is not destroyed by photolysis is decomposed by the aqueous base upon development of the "light" areas. DNQ's in the "dark" areas are removed by non-aqueous means. The photoresist formulation process is entirely non-aqueous. No DNQ should ever make it to the aqueous waste.) as a main component with high sodium chloride concentration (>20 kg/m<sup>3</sup> [>2%]), was removed by treatment with hydrogen peroxide and ultraviolet (UV) irradiation, resulting in complete mineralization of the organic compounds (Hou



et al., 2001). The use of chlorine or sodium hypochlorite and hydrogen peroxide in a second step was found to successfully treat wastewaters containing the salt (Iida et al., 2001). In the wastewater from a Japanese plant producing negative photoresist material [\(Negative photoresist materials, with very minor exceptions, do not contain DNQ's and those are 4- sulfo isomers. We are not familiar with this report.\)](#), anaerobic digestion using microbes separated from soils and sludges decomposed >98% of 1,2-naphthoquinone-2-diazido-5-sulfonic acid sodium salt within four days, but degraded only 10% of the derivatives formed by oxidation and photochemical decomposition within 24 days (Hirata et al., 2000).

## 7.0 Human Exposure

Exposure to the DNQ derivatives may occur during the manufacture [\(DNQ esters are handled several times a year for production. Our employees wear Tyvek suits and respirators when handling DNQ ester solids. Handling is nearly always done under strong local ventilation. We assume other manufacturers take similar precautions.\)](#) and use [\(Typically, containers are swiftly changed from "empty" to full, a matter of moving a siphon from one container to another. The only other likely exposure is during the occasional cleaning of equipment. DNQ esters are high molecular weight and are <8% of the formulation. Application of the liquid photoresist, drying the film, functional use and stripping of the photoresist are nearly fully automatic. There is typically no contact with photoresists, and non-contact exposure to DNQ esters is also expected to be zero.\)](#) of products containing the compounds, particularly photolithography processes in the microelectronics industry. No specific information regarding workplace exposures to the DNQ derivatives was available.

## 8.0 Regulatory Status

The four DNQ derivatives in this report are listed on the Toxic Substances Control Act (TSCA) Inventory.

Sodium 1,2-naphthoquinonediazide-5-sulfonate, at a concentration of 100%, is on the list of self-reactive materials authorized for transportation and not subject to the approval provisions in Section 173.124(a)(2)(iii) (49 CFR 173.224) (DOT, 1998). Under the dangerous goods regulation of the International Maritime Organization, the compound is not accepted in self-reactive solid type D substances (UN No. 3226) (IMO, undated).

Under the Superfund Amendments and Reauthorization Act (SARA) Title III Sections 311-312 (40 CFR 370.21), 1,2-naphthoquinonediazide-5-sulfonyl chloride is not an acute or chronic health hazard, and no sudden releases are expected. It is, however, a flammable and reactive hazard. The substance is also subject to disposal regulations (40 CFR 262 [Hazardous Waste Numbers: D001, D003]) and transportation regulations (40 CFR 172.101 [proper shipping name: Self-reactive solid type B; UN No. 3222]) (MSDS-OHS, 2001a).

Under SARA Title III Sections 311-312 (40 CFR 370.21), 2,3,4-trihydroxybenzophenone tris(1,2-naphthoquinonediazide-5-sulfonate) and 2,3,4-trihydroxybenzophenone 1,2-naphthoquinonediazide-5-sulfonate are not hazards in the following categories: acute or chronic health, fire, reactive, and sudden release (MSDS-OHS, 2001b,c). Under the International Maritime Dangerous Goods (IMDG) code, both compounds have a UN number of 3226 (IMO, 2001).

**9.0 Toxicological Data** [\(We have some basic, and very old, data on the two DNQ esters. See attachment to further communications. Certainly other manufacturers have such data also.\)](#)

## 9.1 General Toxicology

### 9.1.1 Human Data

Acute or short-term exposure to 1,2-naphthoquinonediazide-5-sulfonyl chloride may be irritating to the skin and the eyes (MSDS-OHS, 2001a).

### 9.1.2 Chemical Disposition, Metabolism, and Toxicokinetics

No data were available.

### 9.1.3 Acute Exposure

Acute toxicity values for 1,2-naphthoquinonediazide-5-sulfonyl chloride are presented in the table below.

**Table 1. Acute Toxicity Values for 1,2-Naphthoquinonediazide-5-sulfonyl Chloride**

Route	Species (sex and strain)	LD <sub>50</sub>	Reference(s)
oral	mouse (sex and strain n.p.)	>3200 mg/kg (11.91 mmol/kg)	Eastman Kodak Co. (1992)
	rat (sex and strain n.p.)		
i.p.	mouse (sex and strain n.p.)	200 mg/kg (0.744 mmol/kg)	
	rat (sex and strain n.p.)	400 mg/kg (1.49 mmol/kg)	

Abbreviations: i.p. = intraperitoneal(ly); LD<sub>50</sub> = lethal dose for 50% of test animals; n.p. = not provided

When rats and mice received an i.p. administration of the LD<sub>50</sub> values for 1,2-naphthoquinonediazide-5-sulfonyl chloride, deaths occurred between four hours and three days. Surviving rats had rough coats, while surviving mice (except for two animals) had normal weight gain. When applied to the eyes of rabbits, the compound (100 mg; 0.372 mmol) caused slight to moderate irritation (i.e., erythema); two weeks later, all eyes were normal. When held in contact with the depilated skin of guinea pigs for 24 hours, 1,2-naphthoquinonediazide-5-sulfonyl chloride (0.25, 0.50, or 1.0 mg/kg [0.93, 1.9, 3.7  $\mu$ mol/kg] body weight) produced slight edema and staining. After one week, desquamation and staining were observed. After two weeks, only staining was still present (Eastman Kodak Co., 1992).

### 9.1.4 Short-term and Subchronic Exposure

1,2-Naphthoquinonediazide-5-sulfonyl chloride, incorporated (50% w/v) into a mixture of alcohol:glycerine (1:9 v/v) and applied to the clipped backs of guinea pigs at a rate of 0.5 mL/pig/day for ten days produced moderate to strong erythema associated with slight to moderate edema and numerous raised eschars (Eastman Kodak Co., 1992).

Male Charles River CD, COBS outbred rats fed 1,2-naphthoquinonediazide-5-sulfonyl chloride (0.1% or 1.0% w/w [up to 1000 mg/kg/day]) for 11 days had increased weight gain (109 and 103 g, respectively, for test animals versus 94 g for controls), mean hemoglobin concentrations, hematocrit, white blood cells, as well as slightly elevated serum levels of glutamic oxalacetic transaminase, lactic dehydrogenase, alkaline phosphatase, and urea nitrogen. The mean relative

liver weights of the test animals were slightly lower than controls (12.09% and 11.88% for the 0.1% and 1.0% groups versus 12.66% for controls) (Eastman Kodak Co., 1992).

#### **9.1.5 Chronic Exposure**

No data were available.

#### **9.1.6 Synergistic/Antagonistic Effects**

No data were available.

#### **9.1.7 Cytotoxicity**

No data were available.

#### **9.2 Reproductive and Teratological Effects**

No data were available.

#### **9.3 Carcinogenicity**

No data were available.

#### **9.4 Initiation/Promotion Studies**

No data were available.

#### **9.5 Anticarcinogenicity**

No data were available.

#### **9.6 Genotoxicity**

No data were available.

#### **9.7 Cogenotoxicity**

No data were available.

#### **9.8 Antigenotoxicity**

No data were available.

#### **9.9 Immunotoxicity**

1,2-Naphthoquinonediazide-5-sulfonyl chloride was a potent skin sensitizer in guinea pigs. The animals were sensitized with injection of a compound-heparinized-whole-rabbit-blood reaction product into the footpads; subsequent challenge was by topical application of a solution of the compound (Eastman Kodak Co., 1992). No other data (e.g., dose) were provided.

#### **9.10 Other Data**

No other data were available.

### **10.0 Structure-Activity Relationships**

Many other DNQ derivatives were identified, most of apparent little commercial importance. (See **Table 2** in Appendix B.) A gavage LD<sub>50</sub> value of 8125 mg/L was reported for 1,2-naphthoquinonediazide-5-sulfonic acid [4857-48-1] in rats (Andrianov, 1987). Using the

MultiCASE expert system to predict estrogen receptor binding capacity of a series of compounds, 1-diazonaphthoquinone-4-sulfonic acid [4857-47-0 or 887-76-3] was found to be inactive. Its relative binding activity (RBA) value was  $<0.001$ ; the probability of the prediction being correct was 56% (Klopman and Chakravarti, 2003). No toxicity data were available for any of the other compounds.

PRODUCT	DATE	TEST	RESULT	NOTES			
68510-93-0	09/11/81	oral rat LD 50 female	>5000 mg/kg	in German			
68510-93-0	09/03/81	skin irritation	slightly irritating	in German			
68510-93-0	09/03/81	mucous membrane(eye) irr.	non irritating	in German, same report as skin irritation			
68510-93-0	01/29/82	Ames test	negative	English, Hoechst Pharma (in house), no GLP statement			
68510-93-0	05/30/89	OECD 203 fish toxicity (zebrafish)	CO 22, LC50 22-50, LC100 100 mg	4.1% linters, German, 48 and 96 hr.			
68510-93-0	?	Biodegradation (OECD 301D)	20-60%	in German, notification of German result, not in US file			
5610-94-6	04/08/82	oral rat LD50	>5000	in German, notification of 1982 report, probably 34% Celite, not in US file			
5610-94-6	03/04/82	skin irritation rabbit	non-irritating	in German, notification of 1982 report, probably 34% Celite, not in US file			
5610-94-6	03/04/82	eye irritation rabbit	non -irritating	in German, notification of 1982 report, same report as above. probably 34% Celite. Not in US file.			
5610-94-6	04/26/82	Ames screen	negative	English probably, notification of 1982 report, probably 34% Celite, not in US file			
5610-94-6	12/11/87	Chromosome aberrations, iv	negative	in German, notification of 1982 report, probably 34% Celite, not in US file			
5610-94-6	05/11/89	fish toxicity (zebrafish)	LC 50 48&96 hr >500 mg/l	in German, notification of 1982 report, probably 34% Celite, not in US file			